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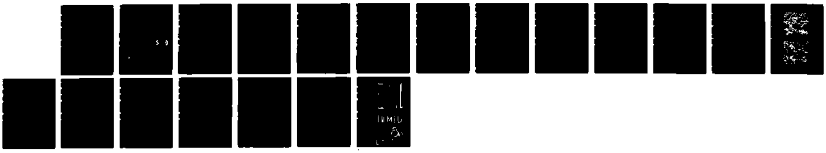

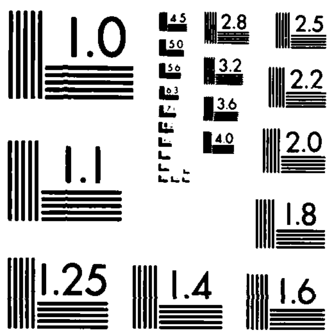

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F49620-83-C-0003

NON-LINEAR OPTICAL TECHNIQUES FOR VISIBLE AND UV LASERS AND THIN FILM DEPOSITION

for the Period

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Prepared for

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November 1985

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19.
Key Words: films, semiconductor, laser-assisted, ultraviolet, aluminum, germanium, impurities

20.
Abstract:

Thin Metal films have been deposited by a multiphoton ionization technique. Laser-initiated semicond~~o~~uctor thin-film growth has been demonstrated and laser irradiation of the substrate~~d~~ has produced higher quality films than that obtained by growth without the laser. Also, laser induced breakdown (LIB) has been shown to be a highly sensitive technique for detecting minute impurities. In addition, a significant improvement in XeCl laser energy output has been realized by the injection of a low intensity UV laser pulse into the XeCl laser cavity.

TABLE OF CONTENTS

I. INTRODUCTION

The goal of the research that was carried out under this AFOSR contract was to demonstrate and develop novel optical approaches to growing metal and semiconductor films as well as new sources of coherent radiation having wavelengths below ~ 0.5 μm. Most of the effort was directed into the first of these two areas and this work has been (we believe) quite fruitful. In the next Section, the results obtained in the last fiscal year (FY'85) will be described. Several spin-offs of this work have also yielded interesting results and these will be described in Section II as well.

II. EXPERIMENTAL RESULTS: FY'85

A. Metal Film Deposition

In an article that was published in early 1984 in the Journal of Chemical Physics, Mitchell and Hackett[1] showed that the multiphoton ionization (MPI) spectra of most of the Column III alkyls (except for $B(C_2H_5)_3$) are identical to those for the respective Column III metal vapors. The MPI spectrum of $Ga(CH_3)_3$, for example, is identical to that for Ga metal vapor. This significant result provides a simple means for selectively depositing a particular Column III film at room temperature.

Figure 1(a) shows (for example) the low-resolution MPI spectrum of $Al_2(CH_3)_6$ that was measured in reference 1. Part

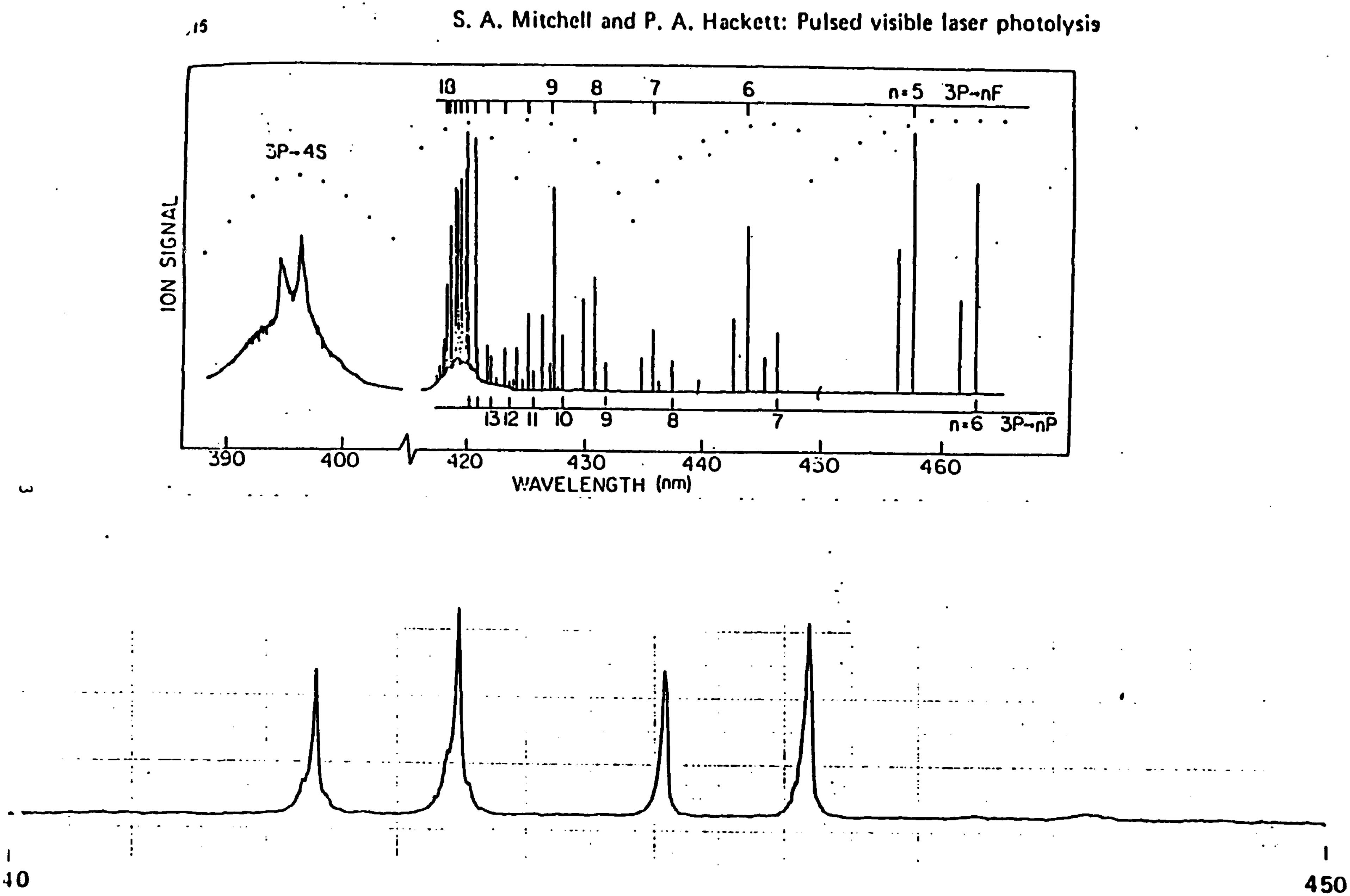


Figure 1. (top) MPI spectrum of TMA in the blue (after reference 1) and (bottom) expanded view of the region between 440 nm and 450 nm (acquired in our laboratory).

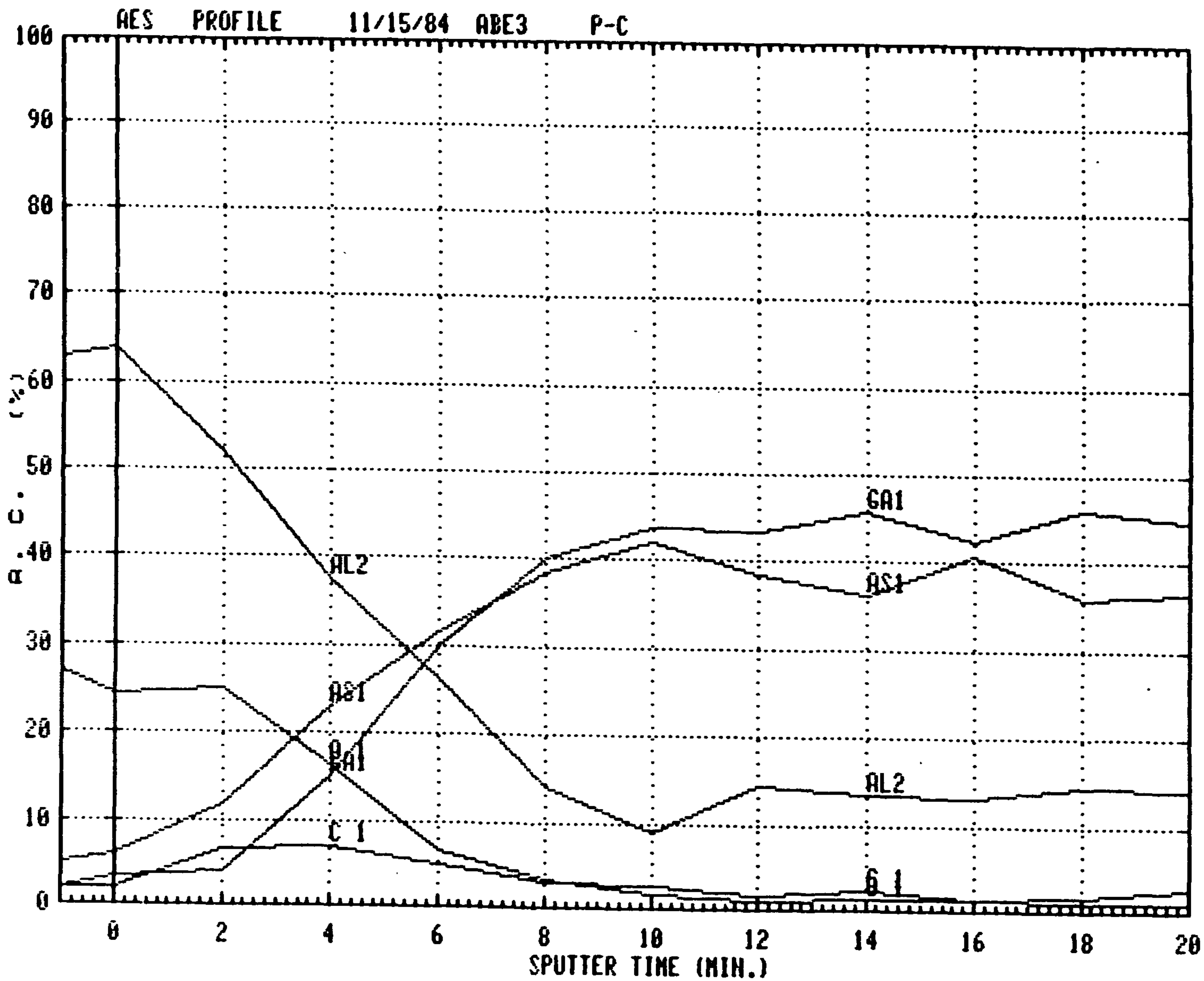


Figure 2. AES depth profile of a 100 Å thick Aℓ film deposited on GaAs by the MPI of TMA.

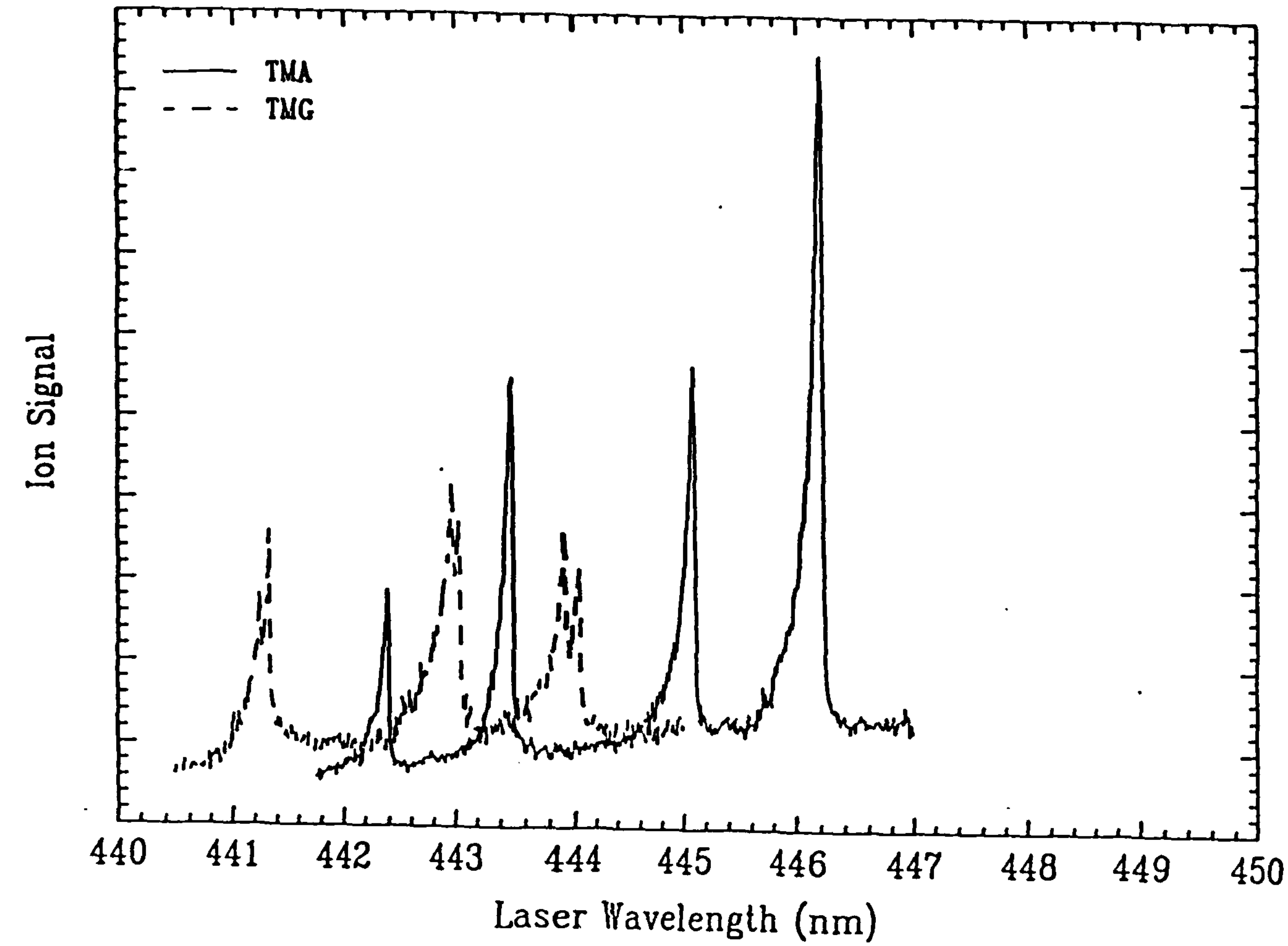


Figure 3. MPI spectra of both TMA and TMG, showing distinct resonances.

(b) of the Figure shows the portion of the spectrum between 440 and 450 nm that was recorded under much higher resolution in our laboratory. The shape of each of the peaks is partially due to the laser intensity (power broadening) and partially to the fine structure of the atomic states involved. We have used several of these resonances to grow thin Al films on GaAs. Doped GaAs substrates were mounted (using liquid indium) to one of two electrodes which were mounted in a quartz cell having a rectangular cross-section. $Al_2(CH_3)_6$ (Trimethylaluminum: TMA) vapor flowed through the cell and between the two electrodes. A pulsed, blue dye laser beam was focussed to a point between the electrodes and ~10^{13} ions were collected per pulse when the dye laser was tuned to one of the MPI resonances shown in Figure 1. Figure 2 is an Auger (AES) depth profile of one of the Al films deposited on GaAs. The film thickness is less than 100Å thick which is well suited for the fabrication of quantum well structures. Note also the low carbon concentration which is gratifying considering the poor base vacuum (~ 10^{-2} mbar) used in these experiments.

The MPI spectrum for trimethylgallium (TMG) was also obtained and is shown in comparison to the TMA spectrum in Fig. 3. Consequently, the distinct MPI peaks of the two metal donors suggest that thin quantum well structures could be grown by using the wavelength agility of a dye laser to selectively deposit a particular metal.

B. Column IV Semiconductor Growth

The focus of this work is the growth of single crystal semiconductor films on various substrates and the eventual fabrication of electronic devices with carefully controlled doping and interface properties. Our initial work has concentrated on the growth of germanium, primarily because of its small bandgap (0.67 eV) and its lattice match to GaAs.

Recent experiments have demonstrated that growth of polycrystalline Ge on GaAs below the pyrolytic threshold can be initiated by laser irradiation of a substrate. An Arrhenius plot, shown in Figure 4, illustrates the results of these experiments, where the vertical line at 718°K indicates the pyrolytic threshold for GeH_4 in this reactor. Currently, experiments are being performed to further characterize and quantify the laser initiated growth.

Also, films have been grown above the pyrolytic threshold both with and without laser irradiation of the substrate. Although results of these studies are preliminary, films grown in the presence of laser radiation exhibit smaller, more regular grains and fewer voids than those grown without the laser. SEM micrographs in Figure 5 illustrate these findings.

C. Impurity Detection by Laser Induced Breakdown The detection and removal of impurities present in semiconductor-bearing gases at the sub-ppm level limit the quality of material obtainable by CVD and MOCVD, in

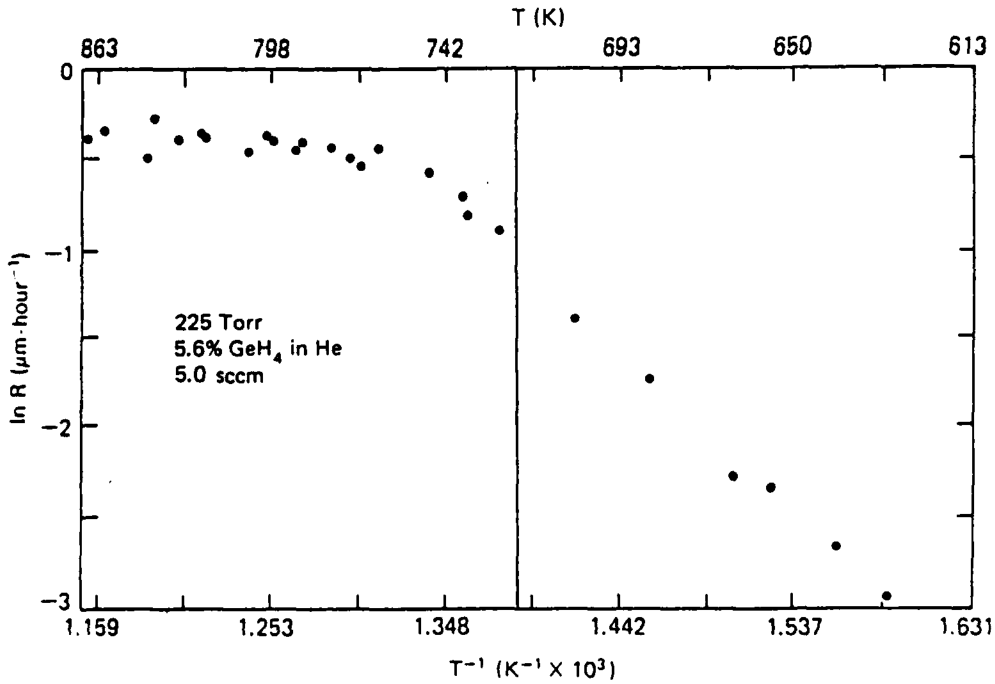
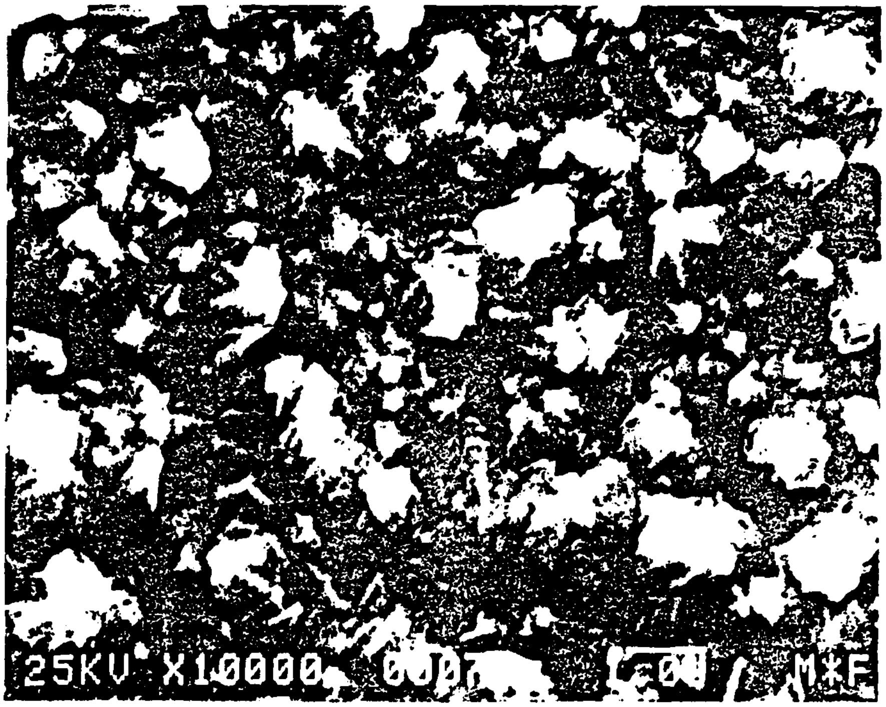
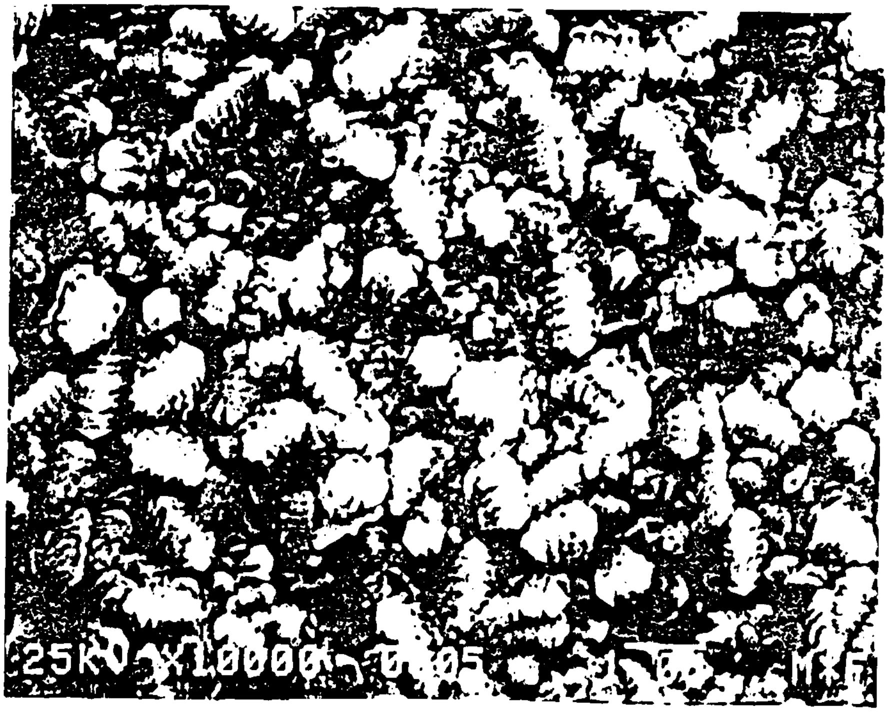


Figure 4. Arrhenius Plot Showing Laser Initiated Chemical Vapor Deposition Below 718 K.



(a) Laser Off



(b) Laser On

Figure 5. Comparison of Ge films grown with and without laser irradiation of the substrate.

particular. High purity GaAs, for example, consistently shows the presence of Si, S and Ge and recent evidence acquired by Professor G. E. Stillman here at the University of Illinois strongly suggests that the Ge is introduced to the system by the AsH_3 used in his VPE reactor. However, it has not yet been possible to confirm this by conventional mass spectrometric techniques since its sensitivity is limited to ~ 1 ppm. Optical techniques offer the promise of being 2 to 3 orders-of-magnitude more sensitive and we have initiated an experimental program to detect impurities at the 1-10 ppb level by laser induced breakdown (LIB).

LIB is a straightforward and sensitive technique for impurity detection. Workers at Los Alamos were the first to show the utility of LIB in this area by examining the exhaust from a pilot coal gasification plant for various impurities. We have done some preliminary experiments in this area with the goal of eventually installing a computer-controlled spectroscopic system on a VPE or MOCVD reactor here at the University of Illinois, dedicated solely to impurity detection.

Figure 6 shows a section of the LIB spectrum of GeH_4 (diluted in He) in the visible. Two emission lines of Ar are obviously present around 522 nm. The significance of this is that the manufacturer specifies that the concentration of Ar in this mixture is $\lesssim$ 1 ppm. Furthermore, no signal averaging techniques were used to obtain this spectrum. Therefore, it is expected that an

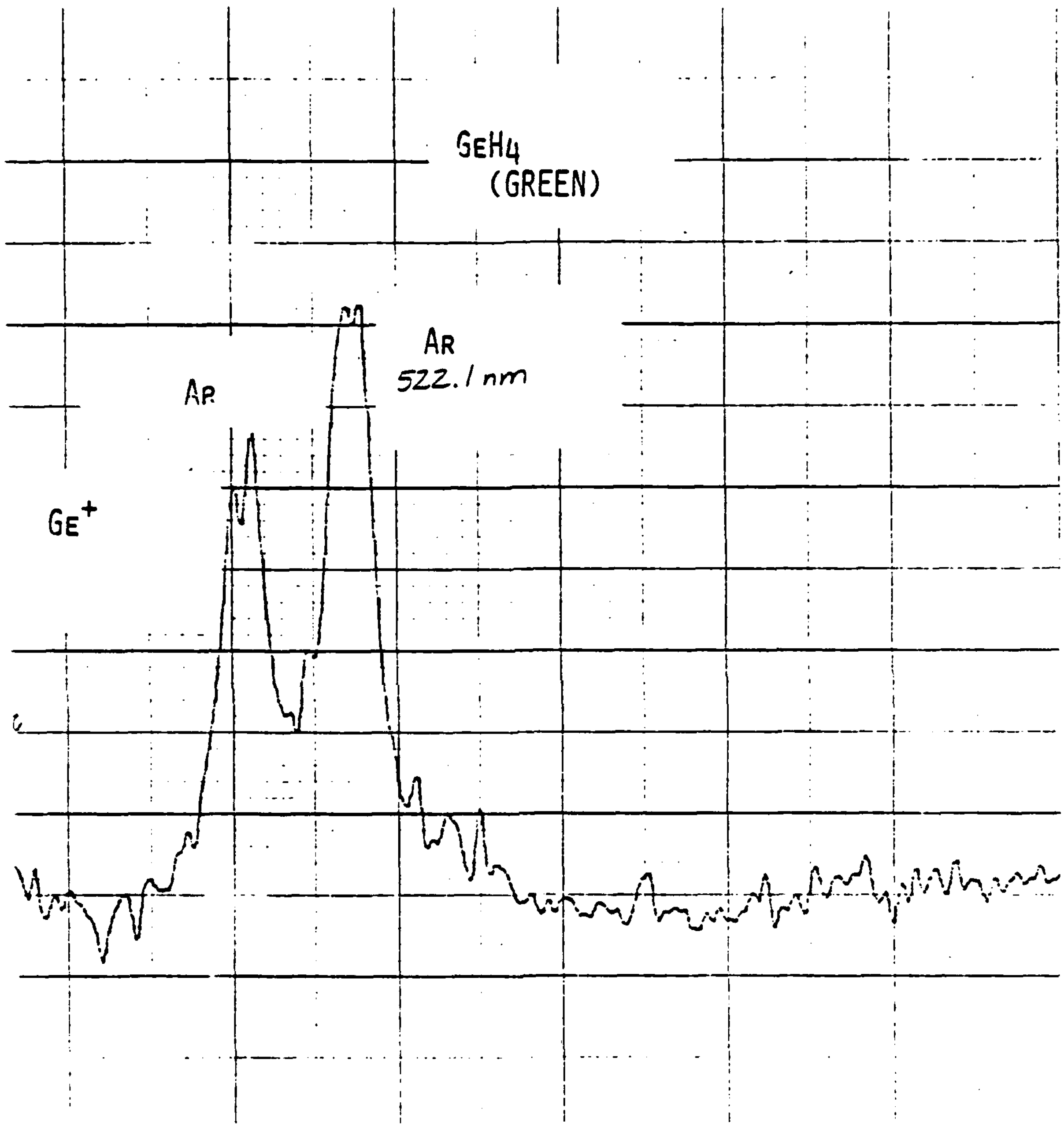


Figure 6. LIB spectrum of 5% GeH_4/95% He mixture in the green showing the presence of Ar.

additional order of magnitude improvement in the S/N ratio can yet be obtained. The next section describes other exeriments that are envisioned in this area.

Related experiments have demonstrated that 1 part per billion (ppb) inpurities of CO_2 in He can be detected by this technique as indicated by the results shown in Figure 7.

D. Spinoffs: Enhanced Rare Gas-Halide Laser Efficiencies

The enhancement of an XeCl laser output energy by the injection of low energy uv laser pulse has been characterized, and the results have recently been published in the Journal of the Optical Society of America B. As indicated in Figure 8, net increases of ~ 25% in the XeCl laser energy can be obtained by the injection of only 5-7 mJ of ArF laser radiation. Also, it appears that this approach will be useful for KrF and several of the other excimer lasers as well. Of course, this has significant implications for DOD since such a large improvement in efficiency can be obtained for a minor investment.

Details of the results obtained in these experiments are given in the attached reprints.

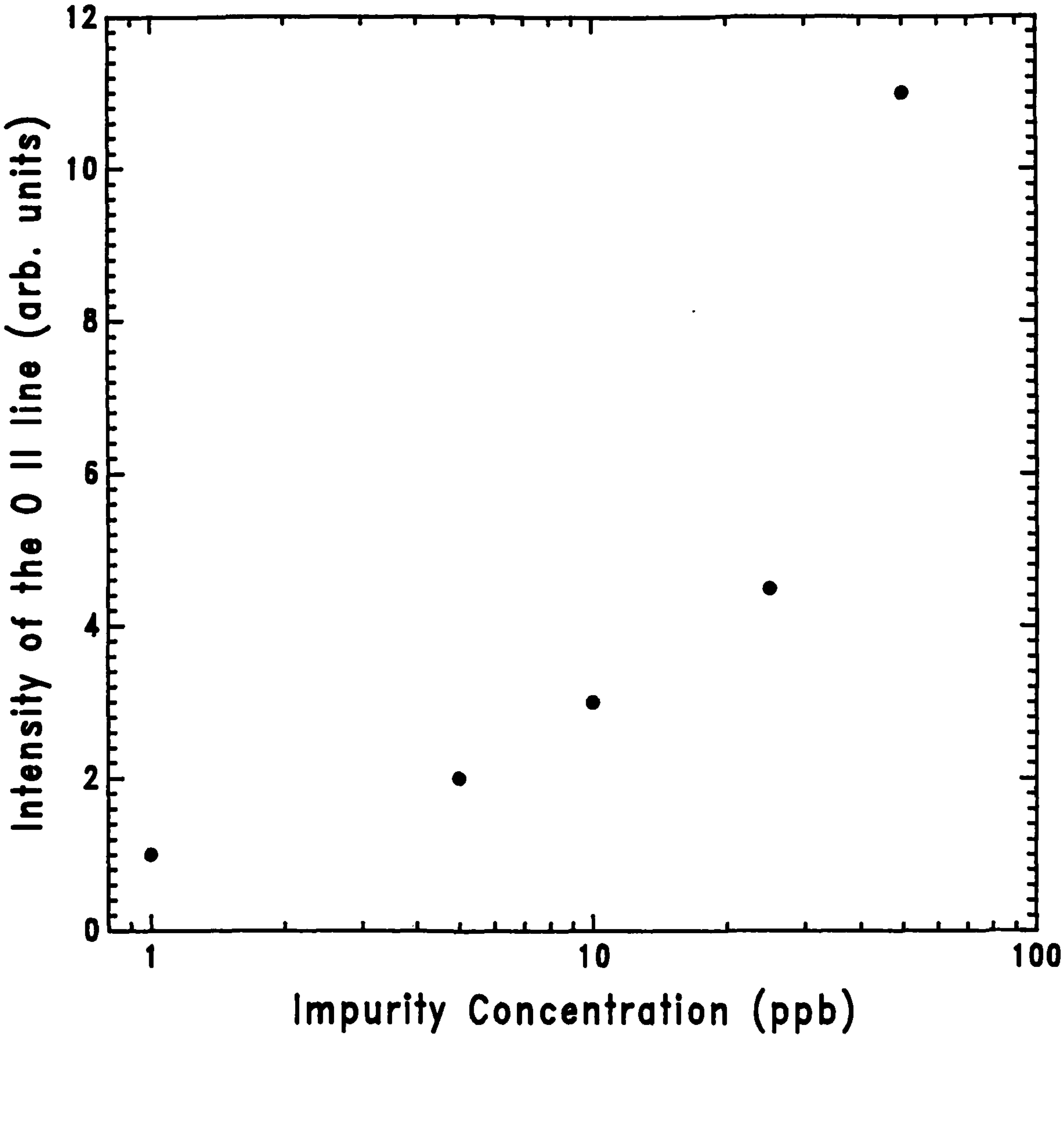


Figure 7. Sensitivity of LIB detection of a CO_2 impurity in He. The emission line being monitored is the OII line at 486.1 nm.

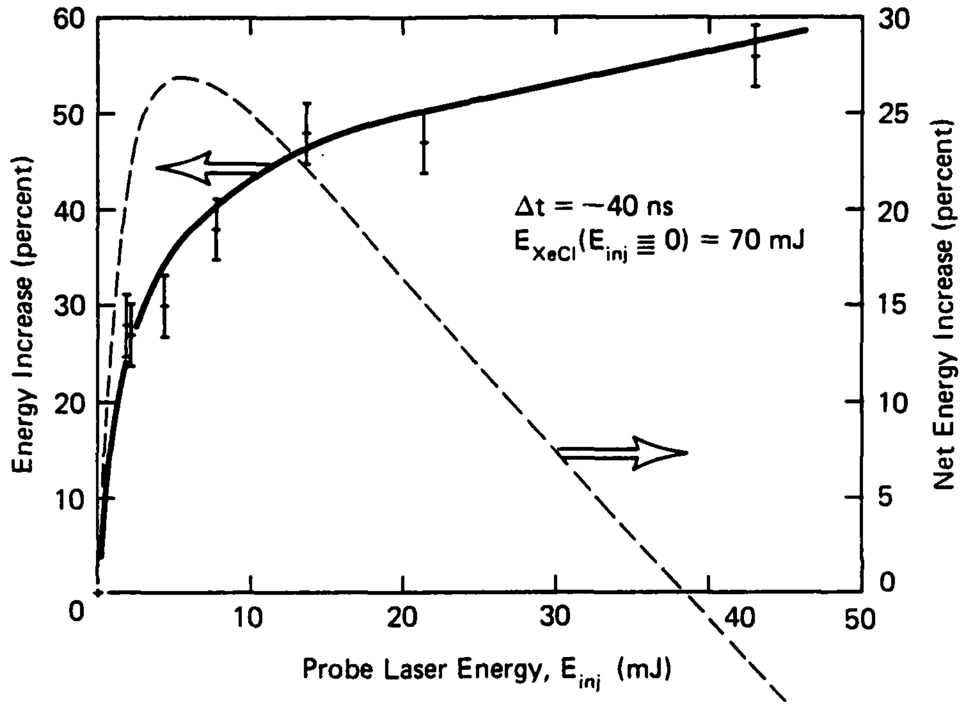


Figure 8. XeCℓ laser enhancement by lower energy UV laser injection.

PAPERS PUBLISHED IN FY '85

1. D. E. Johnson and J. G. Eden, "KXe excimer absorption and S → D, S → F collision induced satellites in K-Xe mixtures," J. Chem. Phys. 82, pp. 2927-2934 (1985).

2. J. F. Osmundsen, C. C. Abele and J. G. Eden, "Activation energy and spectroscopy of the growth of germanium films by ultraviolet laser-assisted chemical vapor deposition," J. Appl. Phys. 57, pp. 2921-2930 (1985).

3. D. E. Johnson and J. G. Eden, "Continua in the visible absorption spectrum of K_2," J. Opt. Soc. Am. B 2, pp. 721-728 (1985).

4. D. B. Geohegan, A. W. McCown and J. G. Eden, "Interaction of ultraviolet laser radiation with a XeCℓ laser," J. Opt. Soc. Am. B 2, pp. 925-930 (1985).

5. J. G. Osmundsen, C. C. Abele and J. G. Eden, "Multiphoton dissociation of GeH_4: Ultraviolet emission spectrum of GeH, J. Chem. Phys. 83 pp. 2159-2161 (1985).

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C. C. Abele, M.S. (E.E.); Thesis Title: "Metal Film Deposition on GaAs by Multiphoton Ionization of Column III Alkyls," September 1985.

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PATENTS APPLIED FOR

J. G. Eden, A. W. McCown and D. B. Geohegan, "Rare Gas-Halide Laser Power Enhancement Device," U.S. Patent Application Serial No. 702, 547.

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